

Hydrogen atom in a spherical well: linear approximation

David Djajaputra and Bernard R. Cooper

Department of Physics, West Virginia University, PO BOX 6315, Morgantown, WV 26506, USA

(February 2, 2008)

We discuss the boundary effects on a quantum system by examining the problem of a hydrogen atom in a spherical well. By using an approximation method which is linear in energy we calculate the boundary corrections to the ground-state energy and wave function. We obtain the asymptotic dependence of the ground-state energy on the radius of the well.

I. INTRODUCTION

The problem of a hydrogen atom confined in a sphere has quite a long history in quantum physics. It was first investigated more than sixty years ago by Michels, de Boer, and Bijl [1] in their study of the effects of pressure on the polarizability of atoms and molecules. This problem was then taken up by Sommerfeld and Welker [2] who studied the problem in detail and calculated the critical radius for which the binding energy becomes zero. Over the years there has been a steady flow of papers on this and other closely related problems. [3–11] The model has often been used as a test problem for various perturbation methods. Using their boundary perturbation method, Hull and Julius [12] obtained a formula which expresses the change of energy for the eigenstates in the confined system in terms of the corresponding wave functions in free space. This method has been improved and generalized by many authors. [13,14] Some variational methods have also been used to study this problem. [15–17] Fröman, Yngve, and Fröman have developed the phase-integral method as a general method to attack the problem of confined quantum systems and their 1987 paper [18] provides 80 references on this problem.

In recent years there has been some renewed interest on this problem. [19,20] This is partly driven by the technological advances, such as in the field of semiconductor quantum dots, [21] that have enabled the construction of interesting nanostructures which contain a small and controllable number (1-1000) of electrons. The computation of the electronic structure of such systems necessarily has to take into account the presence of the finite confining boundaries and their influence on the system.

In this paper we shall study the boundary corrections for a hydrogen atom in a spherical well using an approximation method which is linear in energy. This is a well-known method in solid-state physics and has been widely used in electronic structure calculations, under the name of Linear Muffin-Tin Orbital (LMTO) method, [22] since its initial introduction by O. K. Andersen in 1975. [23,24] The method is best applied to the calculations of the wave functions of a hamiltonian with energies which are in close vicinity of the energy of a known wave function. To the best of our knowledge, this simple method has

never been applied previously to this problem of hydrogen atom in an impenetrable sphere. The present paper seeks to serve two purposes. First, it presents a new approach, which has some pedagogical simplicity, to the confined hydrogen atom problem. Second, it offers an analytically tractable problem from which one can hopefully gain some insights into the workings and the accuracy of the LMTO method.

II. LINEAR METHOD

In this paper we will examine the boundary corrections for a hydrogen atom situated at the center of a spherical cavity of radius S as shown in Fig.1. We will assume the wall of the cavity to be impenetrable and consider the following spherically-symmetric potential:

$$V(r) = \begin{cases} -e^2/r, & r < S, \\ \infty, & r > S. \end{cases} \quad (1)$$

The radius of the cavity will be assumed to be much larger than the Bohr radius: $S \gg a_0$. In the remainder of the paper we shall use the atomic units:

$$\hbar = \frac{e^2}{2} = 2m = 1. \quad (2)$$

The unit of length is the Bohr radius $a_0 = \hbar^2/me^2$ and the unit of energy is the Rydberg: $\text{Ry} = e^2/2a_0 = 13.6$ eV. The Schrödinger equation takes the following form:

$$H\Psi(\mathbf{r}) = \left(-\nabla^2 - \frac{2}{r} \right) \Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \quad (3)$$

The wave function $\Psi(\mathbf{r})$ satisfies the Schrödinger equation for the hydrogen atom for $r < S$, in particular it should still be regular at the origin. The only difference from the free-space case is that now we have to impose a different boundary condition: the wave function should vanish at $r = S$ instead of at $r = \infty$.

For $S \gg a_0$, the changes in the ground-state wave function and energy due to the presence of the wall are expected to be “small” because the wave function is concentrated at the center of the cavity, far away from the confining wall.

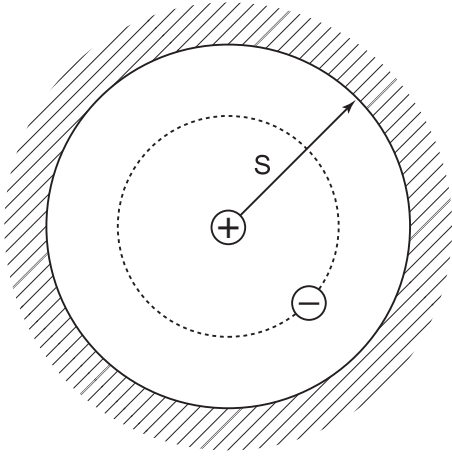


FIG. 1. Hydrogen atom in a spherical well of radius S .

In free space, i.e. in the absence of the confining cavity, the hydrogen atom has the familiar Rydberg spectrum:

$$\varepsilon_n = -\frac{1}{n^2}, \quad n = 1, 2, \dots \quad (4)$$

In the presence of the cavity, we write

$$E_n = \varepsilon_n + \Delta\varepsilon_n. \quad (5)$$

We use small letters (ε, ψ , etc.) to denote quantities for the free-space problem and capital letters (E, Ψ , etc.) for the corresponding quantities in the cavity problem. The dimensionless parameter ($\Delta\varepsilon_n/\varepsilon_n$) is expected to be small for $n^2 a_0 \ll S$. In the linear method, the (unnormalized) wave function at energy E_n is approximated by

$$\Psi(E_n, \mathbf{r}) = \psi(\varepsilon_n, \mathbf{r}) + \Delta\varepsilon_n \dot{\psi}(\varepsilon_n, \mathbf{r}). \quad (6)$$

Here $\dot{\psi}(\varepsilon_n, \mathbf{r})$ is the derivative with respect to energy of $\psi(\varepsilon, \mathbf{r})$ evaluated at $\varepsilon = \varepsilon_n$:

$$\dot{\psi}(\varepsilon_n, \mathbf{r}) = [\partial\psi(\varepsilon, \mathbf{r})/\partial\varepsilon] (\varepsilon = \varepsilon_n). \quad (7)$$

The eigenfunctions in the cavity problem are then obtained by imposing the boundary condition at $r = S$:

$$\Psi(E_n, S, \hat{\mathbf{r}}) = 0, \quad (8)$$

which gives an expression for the energy correction:

$$\Delta\varepsilon_n = -\frac{\psi(\varepsilon_n, S, \hat{\mathbf{r}})}{\dot{\psi}(\varepsilon_n, S, \hat{\mathbf{r}})}. \quad (9)$$

Here $\hat{\mathbf{r}} = (\theta, \phi)$ is a unit vector in the direction of \mathbf{r} .

To apply the linear approximation method we need the general solution to the Schrödinger equation at an arbitrary energy E . Since we are dealing with a spherically-symmetric system, we can separate the variables:

$$\Psi(\mathbf{r}) = R(r)Y_{lm}(\hat{\mathbf{r}}). \quad (10)$$

The resulting radial differential equation is

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right] R = 0. \quad (11)$$

Transforming the variables by defining

$$\omega = \sqrt{-E}, \quad \rho = 2\omega r, \quad (12)$$

and using the following trial functional form [25]

$$R(\rho) = \rho^l e^{-\rho/2} u(\rho), \quad (13)$$

then gives us the following differential equation [25]

$$\rho u'' + [2(l+1) - \rho] u' - [l+1 - \frac{1}{\omega}] u = 0, \quad (14)$$

which is the equation for the confluent hypergeometric function. The general solution of this equation, which is regular at the origin, is [25]

$$u(\rho) = A {}_1F_1\left(l+1 - \frac{1}{\omega}; 2l+2; \rho\right), \quad (15)$$

where A is a normalization constant. The radial part of the general solution to the Schrödinger equation Eq.(3) with energy $E = -\omega^2$ therefore is

$$R_l(\omega, r) = A (2\omega r)^l e^{-\omega r} {}_1F_1\left(l+1 - \frac{1}{\omega}; 2l+2; 2\omega r\right). \quad (16)$$

The free-space solution is obtained by requiring that $R(r) \rightarrow 0$ as $r \rightarrow \infty$. From the properties of the hypergeometric functions, [25] this can only happen if $(l+1-1/\omega)$ is a negative integer or zero. This implies that

$$\frac{1}{\omega} = n, \quad l = 0, 1, \dots, (n-1), \quad (17)$$

with n a positive integer. This directly leads to the Rydberg spectrum in Eq.(4).

The function $R_l(\omega, r)$ is plotted in Fig.2 for $l = 0$ and $\omega = 1, 0.98$, and 0.50 . The $\omega = 1$ curve is the ground-state wave function of the hydrogen atom in free space and is nodeless. Here a node of $R_l(\omega, r)$ is defined to be a value of the argument r which gives zero value for the function $R_l(\omega, r)$. As ω is reduced below 1, the wave function acquires a single node which moves from $r = \infty$ to $r = 2a_0$ at $\omega = 0.50$, where it becomes the $(n, l) = (2, 0)$ eigenstate of the hydrogen atom in free space. One therefore can obtain the ground-state wave function and energy of the hydrogen atom in a cavity of radius S by numerically searching for the energy which gives a wave function with a single node at $r = S$. This provides a useful comparison for our approximation.

Since the spherical harmonics are independent of the energy we can recast Eq.(9) into

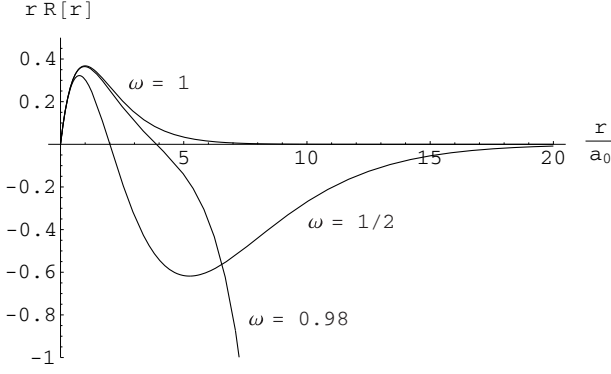


FIG. 2. The function $rR_l(\omega, r)$ as a function of r/a_0 for $l = 0$ and $\omega = 1, 0.98$, and 0.50 . The $\omega = 1$ curve is nodeless. As ω is decreased from 1 to 0.50, the node of the wave function moves from $r = \infty$ to $r = 2a_0$.

$$\Delta\varepsilon_{nl} = 2\omega_n \frac{R_l(\omega_n, S)}{\dot{R}_l(\omega_n, S)}. \quad (18)$$

where $\omega_n = \sqrt{-\varepsilon_n}$ and

$$\dot{R}_l(\omega_n, S) = [\partial R_l(\omega, S)/\partial \omega] (\omega = \omega_n). \quad (19)$$

Substituting the radial function $R_l(\omega, r)$ in Eq.(16) into Eq.(18) then gives us an explicit formal expression for $\Delta\varepsilon_n$ which should be valid for $R \gg n^2 a_0$. Note that the presence of the finite boundary lifts the azimuthal degeneracy of the states with different orbital quantum number l (and the same radial quantum number n). [26] As in the case of the screened Coulomb potential, this occurs because one no longer deal with the pure Coulomb potential. [27,28]

To gain an insight into Eqs.(18)-(19), we shall consider the ground state ($n = 1$), which is a special case of the zero angular momentum ($l = 0$) states. We have

$$R_0(\omega, r) = A e^{-\omega r} {}_1F_1\left(1 - \frac{1}{\omega}; 2; 2\omega r\right). \quad (20)$$

For the ground state ($n = 1$), this is

$$R_0(1, r) = A e^{-r} {}_1F_1\left(0; 2; 2r\right) = A e^{-r}. \quad (21)$$

We are interested in obtaining a simple analytical expression of the correction to the ground-state energy for $S \gg a_0$, therefore we need to calculate the limiting form of $\dot{R}_0(\omega, r)$ for $r \gg a_0$. The asymptotic expansion of the hypergeometric function ${}_1F_1(a, b, z)$ for large z is [29]

$$\frac{{}_1F_1(a, b, z)}{\Gamma(b)} = \frac{e^{i\pi a}}{z^a} \frac{I_1(a, b, z)}{\Gamma(b-a)} + e^z z^{a-b} \frac{I_2(a, b, z)}{\Gamma(a)}, \quad (22)$$

with

$$I_1(a, b, z) = \sum_{n=0}^{R-1} \frac{(a)_n (1+a-b)_n}{n!} \frac{e^{i\pi n}}{z^n} + \mathcal{O}(|z|^{-R}), \quad (23)$$

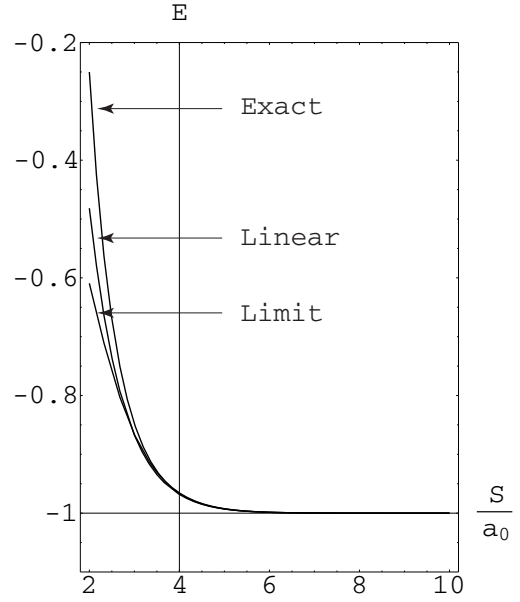


FIG. 3. Dependence of the ground-state energy of a hydrogen atom confined in a spherical cavity on the radius of the cavity S . The topmost curve is the exact result which is obtained by numerically searching for the node of the wave function. The middle curve is obtained from the linear approximation, Eq.(18), using the exact wave function Eq.(21). The lowest curve is obtained using the limiting formula Eq.(31).

$$I_2(a, b, z) = \sum_{n=0}^{R-1} \frac{(b-a)_n (1-a)_n}{n!} \frac{1}{z^n} + \mathcal{O}(|z|^{-R}). \quad (24)$$

The Pochhammer symbol $(a)_n$ is defined by [25]

$$(a)_n = a(a+1) \cdots (a+n-1) = \frac{\Gamma(a+n)}{\Gamma(a)}. \quad (25)$$

We need to calculate the derivative of this function at $a = (1 - 1/\omega)$ with $\omega = 1$. In this case the dominant term comes from the derivative of $\Gamma(a)$ in the second term in Eq.(22). The first term can be neglected because it does not have the exponential term e^z which dominates the derivative at large distances. Keeping only the largest term, we get

$$\frac{\partial}{\partial a} {}_1F_1(a, b, z) \approx -e^z z^{a-b} \Gamma(b) I_2(a, b, z) \frac{\psi(a)}{\Gamma(a)}. \quad (26)$$

Here $\psi(a)$ is the digamma function: $\psi(a) = \Gamma'(a)/\Gamma(a)$. [29] Its ratio with $\Gamma(a)$ as $a \rightarrow 0$ is

$$\lim_{a \rightarrow 0} \frac{\psi(a)}{\Gamma(a)} = \lim_{a \rightarrow 0} \frac{-\gamma - 1/a}{-\gamma + 1/a} = -1, \quad (27)$$

where γ is the Euler constant. This then gives

$$\left[\frac{\partial}{\partial a} {}_1F_1(a, b, z) \right] (a \rightarrow 0) \approx e^z z^{a-b} \Gamma(b) I_2(a, b, z). \quad (28)$$

Using this expression, and keeping only the first two terms in $I_2(a, b, z)$, we can obtain the limiting form of $\dot{R}_0(\omega, r)$ at large r and $\omega \rightarrow 1$:

$$\dot{R}_0(\omega, r) \approx \frac{Ae^{-\omega r}}{\omega^2} \left\{ \frac{e^{2\omega r}}{(2\omega r)^{1+1/\omega}} \left[1 + \frac{\Gamma(2 + 1/\omega)}{2\omega r \Gamma(1/\omega)} \right] \right\}. \quad (29)$$

Exactly at $\omega = 1$, this expression becomes

$$\dot{R}_0(1, r) \approx \frac{Ae^r}{4r^2} \left[1 + \frac{1}{r} \right]. \quad (30)$$

Finally, using this equation and Eq.(21) in Eq.(18), we get the boundary correction to the ground-state energy:

$$\Delta\varepsilon_0(S) \approx 8S(S-1)e^{-2S}, \quad S \gg a_0. \quad (31)$$

III. DISCUSSION

Fig.3 displays the asymptotic dependence of the energy correction on the radius of cavity, Eq.(31), together with the exact curve and the curve obtained from the linear approximation method, Eq.(18), using the exact wave function Eq.(21). It is seen that the asymptotic formula, Eq.(31), is fairly accurate for radii greater than about four Bohr radius. Note that the exact energy at $S = 2a_0$ is equal to $\frac{1}{4}$ Ry, which is the energy of the first excited state $(n, l) = (2, 0)$ of the hydrogen atom in free space. This is because the corresponding wave function has a node at $r = 2a_0$ as can be seen in Fig.2.

The asymptotic formula Eq.(31), which is the limit curve in Fig.3, is a “double-approximation” to the exact curve. It is an asymptotic form of the linear curve, Eq.(18), valid for large values of S/a_0 . The linear curve itself is an approximation, linear in energy, to the exact curve. For small values of S/a_0 , and within the linear approximation method, one has to use Eq.(18) which in general, unfortunately, does not correspond to a simple analytic expression. This does not pose a problem in actual electronic-structure applications because there the wave function and its energy derivative are computed numerically. In this paper, for pedagogical purposes, we have calculated the asymptotic formula, Eq.(31), which does correspond to a simple analytic expression.

Knowing the dependence of the ground-state energy on the cavity radius, Eq.(31), allows us to calculate the pressure needed to “compress” a hydrogen atom in its ground state to a certain size. This is given by

$$p(S) = -\frac{\partial \Delta\varepsilon_0}{\partial V} \approx \frac{4e^{-2S}}{\pi} \left(1 - \frac{2}{S} \right). \quad (32)$$

At $S = 4a_0$ this has a value of 2.13×10^{-4} eV/ a_0^3 = 1.47×10^4 GPa. At this radius, the change of the ground-state energy is 0.032 Ry which is only three percent of the binding energy of a free hydrogen atom.

The information on the effects of the boundary on the wave function of the atom can also be used to study the influence of the boundary on other properties of the atom, e.g., the spin-orbit coupling energy. It is also interesting to calculate the changes in the wave function and energy of the atom when it is displaced from the center of the cavity, and the force that will push it back towards the center. The linear method also seems to be well-suited for the analysis of the “soft-cavity” case where we have a finite potential outside the cavity, instead of the infinite potential considered in this paper. These topics will be examined in future works.

In conclusion, we have used a linear approximation method to calculate the asymptotic dependence of the ground-state energy of a hydrogen atom confined to a spherical cavity on the radius of the cavity. The boundary correction to the energies of the excited states can be obtained using the same method.

Acknowledgements—D. D. is grateful to Prof. David L. Price (U. Memphis) for introducing him to Andersen’s linear approximation method and for many useful discussions. Thanks are also due to Dr. H. E. Montgomery, Jr. for many useful references. This work has been supported by AF-OSR Grant F49620-99-1-0274.

-
- [1] A. Michels, J. de Boer, and A. Bijl, “Remarks concerning molecular interaction and their influence on the polarizability,” *Physica* **4**, 981–994 (1937).
 - [2] A. Sommerfeld and H. Welker, “Künstliche Grenzbedingungen beim Keplerproblem,” *Ann. Phys.* **32**, 56–65 (1938).
 - [3] S. R. de Groot and C. A. ten Seldam, “On the energy levels of a model of the compressed hydrogen atom,” *Physica* **12**, 669–682 (1946).
 - [4] D. Suryanarayana and J. A. Weil, “On the hyperfine splitting of the hydrogen atom in a spherical box,” *J. Chem. Phys.* **64**, 510–513 (1976).
 - [5] E. V. Ludena, “SCF calculations for hydrogen in a spherical box,” *J. Chem. Phys.* **66**, 468–470 (1977).
 - [6] J. A. Weil, “Hydrogen atom in a spherical box. II. Effect on hyperfine energy of excited state admixture,” *J. Chem. Phys.* **71**, 2803–2805 (1979).
 - [7] E. Ley-Koo and S. Rubinstein, “The hydrogen atom within spherical boxes with penetrable walls,” *J. Chem. Phys.* **71**, 351–357 (1979).
 - [8] E. Ley-Koo and S. Rubinstein, “The hydrogen atom inside boxes with paraboloidal surfaces,” *J. Chem. Phys.* **73**, 887–893 (1980).
 - [9] R. LeSar and D. R. Herschbach, “Electronic and vibrational properties of molecules at high pressures. Hydrogen molecule in a rigid spherical box,” *J. Phys. Chem.* **85**, 2798–2804 (1981).

- [10] W. Wilcox, "A formula for energy displacements for the confined hydrogen atom," *Am. J. Phys.* **57**, 526–528 (1989).
- [11] S. Goldman and C. Joslin, "Spectroscopic properties of an isotropically compressed hydrogen atom," *J. Phys. Chem.* **96**, 6021–6027 (1992).
- [12] T. E. Hull and R. S. Julius, "Enclosed quantum mechanical systems," *Can. J. Phys.* **34**, 914–919 (1956).
- [13] K. K. Singh, "Theory of boundary perturbation and the compressed hydrogen molecular ion," *Physica* **30**, 211–222 (1964).
- [14] J. Gorecki and W. B. Brown, "Iterative boundary perturbation method for enclosed one-dimensional quantum systems," *J. Phys. B* **20**, 5953–5957 (1987).
- [15] G. A. Arteca, F. M. Fernandez, and E. A. Castro, "Approximate calculation of physical properties of enclosed central field quantum systems," *J. Chem. Phys.* **80**, 1569–1575 (1984).
- [16] J. L. Marin, S. A. Cruz, "On the use of direct variational methods to study confined quantum systems," *Am. J. Phys.* **59**, 931–935 (1991).
- [17] J. L. Marin, R. Rosas, and A. Uribe, "Analysis of asymmetric confined quantum systems by the direct variational method," *Am. J. Phys.* **63**, 460–463 (1995).
- [18] P. O. Fröman, S. Yngve, and N. Fröman, "The energy levels and the corresponding normalized wave functions for a model of a compressed atom," *J. Math. Phys.* **28**, 1813–1826 (1987).
- [19] Y. P. Varshni, "Accurate wavefunctions for the confined hydrogen atom at high pressures," *J. Phys. B* **30**, L589–L593 (1997), and references therein.
- [20] Y. P. Varshni, "Critical cage radii for a confined hydrogen atom," *J. Phys. B* **31**, 2849–2856 (1998).
- [21] L. Jacak, P. Hawrylak, and A. Wójs, *Quantum Dots*, Springer-Verlag, Berlin, 1998.
- [22] H. L. Skriver, *The LMTO Method*, Springer-Verlag, Berlin, 1984.
- [23] O. K. Andersen, "Linear methods in band theory," *Phys. Rev.* **B12**, 3060–3083 (1975).
- [24] V. Kumar, O. K. Andersen, and A. Mookerjee, *Lectures on Methods of Electronic Structure Calculations*, World Scientific, Singapore, 1994.
- [25] J. B. Seaborn, *Hypergeometric Functions and Their Applications*, Springer-Verlag, New York, 1991, Chapter 6.
- [26] R. W. Shea and P. K. Aravind, "Degeneracies of the spherical well, harmonic oscillator and hydrogen atom in arbitrary dimensions," *Am. J. Phys.* **64**, 430–434 (1996).
- [27] W. Greiner and B. Müller, *Quantum Mechanics: Symmetries*, Springer-Verlag, Berlin, 1994, Chapter 14.
- [28] In group theoretical language, modifications to the pure Coulomb potential break the $SO(4)$ symmetry of the hydrogen atom: the Runge-Lenz *operator* no longer commute with the hamiltonian. This should be contrasted with the classical case where the Runge-Lenz *vector* is still a good constant of motion and the presence of the boundary does not have any effect on the orbit of the particle if it is greater than the orbit's aphelion. Greiner's book [27] gives a detailed discussion on the Runge-Lenz vector and the $SO(4)$ symmetry of the hydrogen atom.
- [29] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York, 1965, Eq.(13.5.1).